

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

11 Publication number:

0051 810  
A1

US 4311629

DQ

12

## EUROPEAN PATENT APPLICATION

21 Application number: 81109130.5

22 Date of filing: 28.10.81

51 Int. Cl.<sup>3</sup>: C 08 G 77/18, C 08 G 77/06,  
C 09 D 5/14, A 01 N 55/04,  
C 08 L 83/08, C 09 D 3/00

30 Priority: 12.11.80 US 206295

43 Date of publication of application: 19.05.82  
Bulletin 82/20

84 Designated Contracting States: DE FR GB IT NL SE

71 Applicant: AMERON, INC., 4700 Ramona Boulevard,  
Monterey Park California 91754 (US)

72 Inventor: Gysegem, Albert Peter, 41359 Sylvester Drive,  
Lebanon Oregon 97355 (US)

74 Representative: Patentanwälte Grünecker, Dr.Kinkeldey  
Dr.Stockmair, Dr.Schumann, Jakob, Dr.Bezold Melster,  
Hilgers, Dr.Meyer-Plath, Maximilianstrasse 43,  
D-8000 München 22 (DE)

54 Method for making antifouling coating composition.

57 A solution containing hydrolyzed organotin siloxane polymeric material is formed by hydrolyzing an organotin R-oxy siloxane in a water miscible solvent; R being an alkyl or alkoxyalkyl group with less than six carbon atoms. A water immiscible solvent is added and the water miscible solvent and R-alcohol from hydrolysis are removed by distillation. A marine antifouling coating can be made when the water immiscible solvent evaporates from the solution. A preferred embodiment hydrolyzes tributyltin ethoxy-siloxane in ethyl alcohol with xylene as the water immiscible solvent.

EP 0 051 810 A1

1

5

13081:RDS

10     METHOD FOR MAKING ANTIFOULING COATING COMPOSITIONField of the Invention

15         This invention relates to making a solution containing hydrolyzed organotin siloxane polymeric material suitable for use in marine antifouling coatings.

20     Background of the Invention

25         Compositions have been developed for protecting marine surfaces from fouling organisms, including a linear or cross-linked polymer having a siloxane backbone and trisubstituted tin radicals such as tributyl tin bonded to silicon atoms by way of an oxygen atom. The biologically active polymer can be used for forming coatings for steel, concrete, or other surfaces exposed to marine environments for inhibiting the growth of fouling organisms. In some 30     embodiments the polymer is present as an additive in a coating composition. In other embodiments the cross-linked polymer forms a portion of the binder of the coating.

35

1 U.S. Patent No. 4,080,190 by Law and Gysegem,  
which is hereby incorporated by reference, discloses  
such compositions with a variety of organotin radicals  
and synthesis techniques. The ratio of tin to silicon  
5 atoms in the polymer can be varied for obtaining  
different properties in the polymer. When the  
proportion of tin is low, a cross-linked polymer can  
be formed by hydrolysis and polycondensation of a  
siloxane-tin precursor. In an exemplary embodiment  
10 the precursor is formed by reaction of tetraethoxysilane  
or a short chain ethoxysiloxane with a carboxylic acid  
derivative containing a tin radical, such as tributyltin  
acetate. A prepolymer can be formed by partially or  
completely hydrolyzing the precursor. Water and a  
15 hydrolysis catalyst such as hydrogen ion or hydroxyl ion  
are added to the solvent. Upon evaporation of the  
solvent polycondensation occurs, yielding the desired  
polymer.

It is sometimes convenient to hydrolyze the  
20 precursor to a prepolymer before completing a coating  
composition since prehydrolysis can reduce the curing  
time of a coating. Polycondensation of the prepolymer  
has heretofore been inhibited by retaining the  
prepolymer in ethyl alcohol or similar solvent. Ethyl  
25 alcohol is a product of hydrolysis of the precursor  
when, for example, an ethoxysilicate is employed in  
the synthesis. When such a coating is applied,  
evaporation of ethyl alcohol results in polycondensation  
in the coating.

30

35

1           Ethyl alcohol and similar water miscible solvents  
may not be compatible with other ingredients in the  
coating composition. This is particularly true when  
the coating composition includes a chlorinated rubber,  
5           for example. It is therefore desirable to provide a  
solution containing polymeric material which is  
compatible with such coating compositions.

10           Brief Summary of the Invention

          Thus, in practice of this invention, a solution  
containing hydrolyzed organotin siloxane polymeric  
material is formed by combining an organotin R-oxy  
siloxane, where R represents a group consisting of  
15           alkyl and alkoxyalkyl radicals containing less than  
six carbon atoms, a water miscible solvent, water,  
a hydrolysis catalyst, and a water immiscible solvent.  
After hydrolysis of the organotin R-oxy siloxane,  
the water miscible solvent and R-alcohol from the  
20           hydrolysis reaction are removed by distillation. The  
water immiscible solvent, such as xylene, is preferably  
added after hydrolysis. Surprisingly, it is found  
that precipitation of such polymeric material does not  
25           occur from the water immiscible solvent.

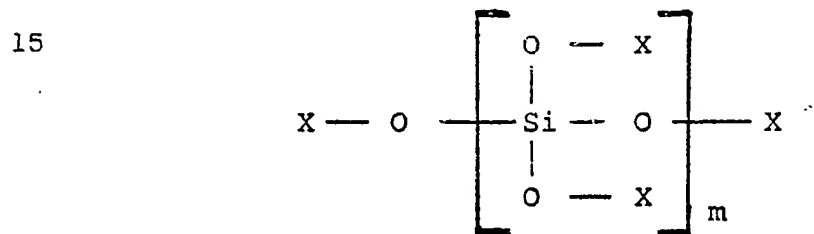
30

35

1 Description

As used herein, the term "precursor" refers to an organotin R-oxy siloxane where R represents a group consisting of alkyl and alkoxyalkyl radicals containing less than six carbon atoms, the term "prepolymer" refers to a precursor that is partly or completely hydrolyzed but not completely condensed; the term "polymer solution" refers to a solution of a water immiscible solvent containing a polymeric material; and the term "polymer" refers to a thoroughly polycondensed prepolymer including linear and/or cross-linked polymers.

Precursors for forming prepolymers for marine antifouling compositions have the formula



20 where m is from about 1 to about 10; where each X is independently selected from the group consisting of R and Y; where each Y in the precursor independently is a trisubstituted tin radical having the formula



30 where  $\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  are independently selected from the group consisting of alkyl, cycloalkyl, and aryl radicals, where  $\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  contain in combination up to about 18 carbon atoms, and where the X's are selected

1 so that the ratio of tin atoms to silicon atoms  
in the precursor is in the range of from about 1:50  
to about 1:1. The Y's in the precursor can be the same  
or different. Depending upon the ratio of tin atoms  
5 to silicon atoms in the precursor and the nature of  
the  $R_1$ ,  $R_2$ , and  $R_3$  groups on the tin, the precursor  
can be a liquid or a waxy solid at room temperature.

In a mixture of precursor molecules, m represents  
the average number of silicon atoms per precursor  
10 molecule. Generally there is a random distribution of  
molecules comprising more and less than m silicon atoms.  
For example, where m equals 5, precursor molecules  
containing predominantly 4, 5 or 6 silicon atoms are  
present. A few molecules with larger and smaller  
15 numbers of silicon atoms can also be present.

In the above formula for the precursors, preferably  
m is less than about 10 so the precursor can be  
polymerized by hydrolysis and polycondensation.  
Preferably m is an average of about five. Such a  
20 material comprises a mobile liquid with a high  $\text{SiO}_2$   
content having ample side groups for substitution of  
tin radicals and subsequent hydrolysis and  
polycondensation. A suitable material is available  
from Union Carbide Chemical Company as "Ethyl Silicate  
25 40". This is an ethyl polysilicate or ethoxysiloxane  
having an average of about five silicon atoms per  
molecule, that is, m equals five, although individual  
molecules may comprise as few as one silicon atom.  
This material has an  $\text{SiO}_2$  content of about 40%.

1 R comprises alkyl and alkoxyalkyl radicals  
containing less than about 6 carbon atoms so that the  
alcohol analog of R formed during hydrolysis of the  
precursor has sufficient volatility for distillation.  
5 Generally, the higher the molecular weight of R, the  
lower the volatility of its alcohol analog. Exemplary  
of the radicals which R can be are methyl, ethyl,  
n-propyl, isopropyl, n-butyl, isobutyl, methyloxymethyl,  
methyloxyethyl, and the like. Preferably X is the ethyl  
10 radical since transesterification yields ethyl acetate  
in a preferred embodiment and hydrolysis yields ethyl  
alcohol, each of which is readily removed by  
distillation.

15  $R_1$ ,  $R_2$ , and  $R_3$  can be lower alkyl radicals containing  
less than about 10 carbon atoms such as methyl, ethyl,  
propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl,  
hexyl, octyl, nonyl, isooctyl radicals, and the like.  
These can also be a substituted lower alkyl radical.  
Substituents include chloride, bromide, ether and aryl  
20 substituents, and the like.

$R_1$ ,  $R_2$ , and  $R_3$  can be a lower cycloalkyl radical  
such as the cyclohexyl radical and substituted lower  
cycloalkyl radicals.

25  $R_1$ ,  $R_2$ , and  $R_3$  can be an aryl radical such as the  
phenyl radical and substituted phenyl radicals.  
Substituents include chloride, bromide, ether, and alkyl  
substituents, and the like. Thus  $R_1$ ,  $R_2$ , and  $R_3$  can be  
chlorophenyl, bromophenyl, nitrophenyl, tolyl, xylyl,  
ethylphenyl, and the like. When  $R_1$ ,  $R_2$ , and  $R_3$  are all  
30 aryl radicals and the precursor has a tin to silicon

1 atom ratio of about 1:5, the prepolymer is a solid  
with only slight solubility in common solvents. Thus,  
if the prepolymer is to be used for forming a binder  
for coating compositions,  $R_1$ ,  $R_2$ , and  $R_3$  generally  
5 cannot all be aryl radicals.

Preferably,  $R_1$ ,  $R_2$ , and  $R_3$  are the same because  
trisubstituted tin compounds where the tin is  
substituted with the same radical are commercially  
available. However,  $R_1$ ,  $R_2$ , and  $R_3$  can be different  
10 such as where Y is the octyl-dimethyl tin radical.

The total number of carbon atoms comprising a  
trisubstituted tin moiety has a large effect on its  
biological activity. The effect appears to be one  
of size rather than chemical or electronic effect.  
15 For example, the octyldimethyl and the tributyl tin  
radicals, which have about the same number of carbon  
atoms, exhibit about the same toxicity toward mammals  
and fouling organisms. In general, small moieties,  
such as the trimethyl tin and triethyl tin radicals,  
20 show only slight toxicity toward bacteria and marine  
fouling organisms, but extremely high toxicity toward  
mammals, including man. Tripropyl tin and tributyl tin,  
on the other hand, exhibit low toxicity toward man,  
but are the most effective trialkyl tin compounds for  
25 antifouling use. As the total number of carbons in a  
trialkyl tin compound increases above about 12 to 14,  
both the human toxicity and antifouling activity  
decrease due to the increase of the total number of  
carbon atoms.

30 Preferably, when  $R_1$ ,  $R_2$ , and  $R_3$  are alkyl radicals,  
the total number of carbon atoms in  $R_1$ ,  $R_2$ , and  $R_3$  in



1 combination is less than about 14 carbon atoms for high  
biological activity. Generally,  $R_1$ ,  $R_2$ , and  $R_3$  contain  
less than about 18 carbon atoms in combination so that  
compositions effective in protecting materials from  
5 growth of marine organisms can be prepared.

Preferably,  $R_1$ ,  $R_2$ , and  $R_3$  are selected so that  
Y is the tributyl, tripropyl, triphenyl or tricyclohexyl  
tin radical. These radicals are preferred because they  
are broad-spectrum toxicants, especially for many marine  
10 organisms, and display minimal toxicity to man. The  
tributyl tin radical is particularly preferred.

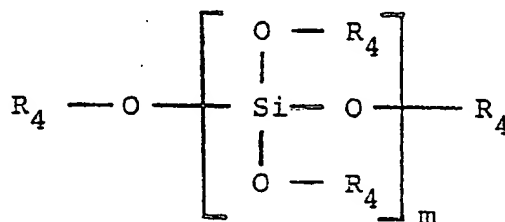
A precursor preferably has a ratio of tin to silicon  
atoms greater than about 1:50 because at ratios less than  
about 1:50 a coating prepared with the prepolymer shows  
15 inadequate biological activity to be of much commercial  
value. The maximum ratio of tin to silicon atoms in the  
precursor is preferably about 1:1. If the ratio is  
higher than about 1:1 steric hindrance by the tin moiety  
may inhibit extensive polycondensation and significantly  
20 limit the molecular weight of the resultant polymer.

The optimum tin to silicon atom ratio of a prepolymer  
used for forming a binder is a balance of competing  
considerations. On one hand, the higher the tin to  
silicon atom ratio, the more effective and more  
25 long-lived is a coating including the prepolymer.  
However, at higher ratios of tin to silicon atoms,  
curing of the prepolymer by hydrolysis and  
polycondensation to form a polysiloxane becomes  
progressively more difficult. At tin to silicon atom  
30 ratios greater than about 2:5, the prepolymer is not  
suitable for preparing binders for coating compositions

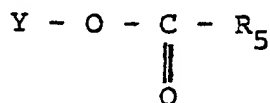
1 because the polymer remains soft and does not cure to  
sufficient hardness to be used as a coating. It is  
believed that a prepolymer having a tin to silicon  
atom ratio greater than about 2:5 is unsatisfactory  
5 for forming binders because the bulky organotin group  
prevents polymerization by either blocking the attack  
of water on the reactive sites of the precursor, or  
by inhibiting condensation of the intermediate silanol  
formed during hydrolysis with another silanol group.

10 A prepolymer for forming a biologically active  
polysiloxane binder preferably has a tin to silicon  
atom ratio of from about 1:12 to about 1:3. In this  
range it has been found that a hard, clear,  
solvent-resistant film exhibiting effective and  
15 long-lived biological activity in preventing fouling  
on marine surfaces can be formed.

The precursor is preferably prepared by reacting  
a silicate having the formula



25 with about n moles per mole of the silicate of a  
carboxylic acid derivative having the formula

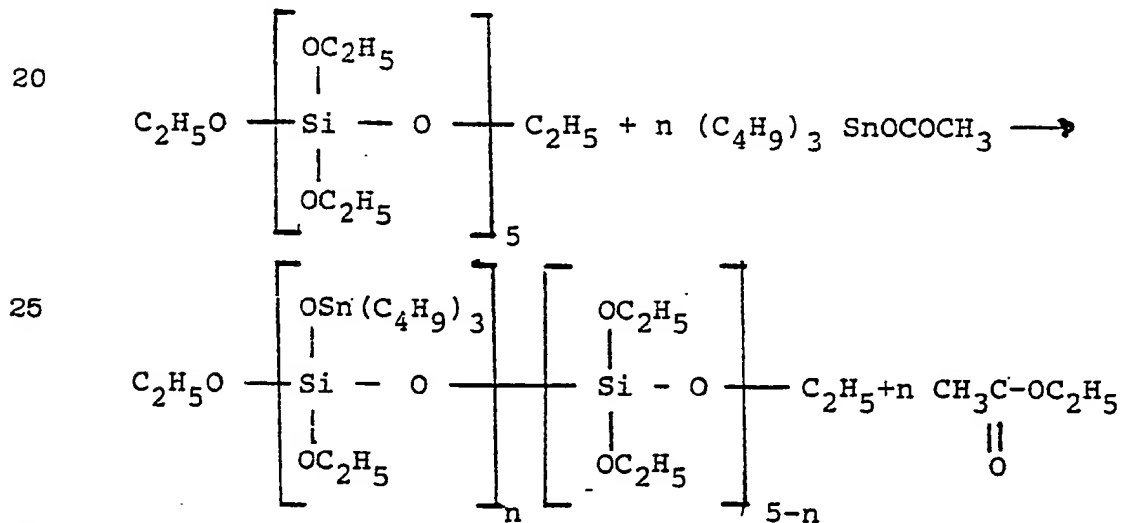


30 where m and Y are as above, and where the ratio of n to m  
is in the range of from about 1:50 to 1:1 to give a  
desired tin to silicon atom ratio as described above.

1  $R_4$  represents the group consisting of alkyl and  
 alkoxyalkyl radicals containing less than about  
 six carbon atoms, i.e.,  $R_4$  is the organic portion  
 of the group from which X is selected. Each  $R_4$   
 5 may be the same or different. Preferably,  $R_4$   
 is the ethyl radical.

$R_5$  is selected from the group consisting of  
 hydrogen, and alkyl, cycloalkyl, and alkoxyalkyl  
 radicals.  $R_5$  is selected for convenience, i.e.,  
 10 so that the carboxylic acid ester formed in the  
 reaction is sufficiently volatile to be removed  
 easily from the product. Preferably a trisubstituted  
 tin acetate is employed.

Exemplary of silicates and carboxylic acid  
 15 derivatives which can be used are "Ethyl Silicate  
 40" and tributyltin acetate. "Ethyl Silicate 40"  
 and tributyltin acetate react according to the  
 equation



30 The tributyltin substituted silicon atoms are randomly  
 located along the chain, and a single silicon atom can  
 be substituted by none, one, two or three tributyltin  
 groups.

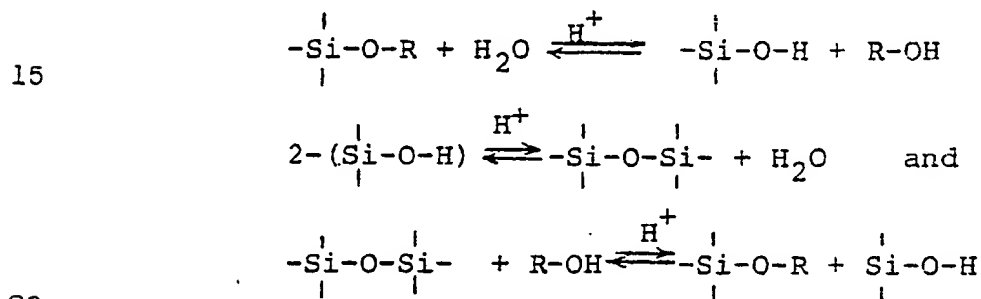
1       The reaction of the silicate and the carboxylic  
acid derivative is conducted at an elevated temperature,  
and at least at a temperature sufficiently high that  
the carboxylic acid derivative melts. The silicate and  
5       carboxylic acid derivative are reacted at a temperature  
below the temperature at which the precursor prepared  
from the silicate and carboxylic acid derivative  
decomposes. Decomposition may be evidenced by darkening  
of the precursor and a hydrocarbon-like odor. For  
10       example, when preparing a precursor from tributyltin  
acetate and Ethyl Silicate 40, the temperature should  
be maintained from about 160 to about 180°C.

      Another method for preparing the precursor is to  
combine a silicate, as described above, with about  $n/2$   
15       moles of water per mole of the silicate and  $n/2$  moles  
per mole of the silicate of a bis-trisubstituted tin  
oxide having the formula  $Y-O-Y$  where  $Y$  and  $n$  have  
the same meaning as above. Generally, a silicate reacts  
at a lower temperature with a tin oxide than with the  
20       carboxylic acid derivative of the tin oxide. For  
example, bis-tributyltin oxide reacts at a fast rate  
with Ethyl Silicate 40 in the presence of water at  
about 85°C compared to the 160°C required when  
tributyltin acetate is used.

25       Another method for preparing the precursors is to  
combine a silicate as described above with about  $n$  moles  
of a trisubstituted tin hydroxide having the formula  
 $Y-OH$ , where  $Y$  and  $n$  have the same meaning above, per  
mole of the silicate. The silicate and tin hydroxide  
30       are combined at a temperature below the temperature at

1 which the precursor formed from the tin hydroxide and  
the silicate decomposes.

The fully polymerized polysiloxane is prepared  
from the precursor by hydrolysis followed by  
5 polycondensation. The hydrolysis of alkylsilicates at  
neutral pH is generally too slow to be able to use the  
silicate as a binder in coating formulations. However,  
in either acidic or basic medium, the rate of hydrolysis  
is appreciably increased. In acid conditions, achieved  
10 by adding small amounts of an acid to the water used in  
the hydrolysis, the equilibrium conditions are reached  
in hours. These equilibrium conditions, which are,



all occur simultaneously. Also under acid conditions,  
the tendency for linear chain extension and cyclization  
is much stronger than for cross-linking. All of these  
account for the liquid nature of the hydrolyzed prepolymer  
25 when in a closed system where no alcohol can escape. In  
the atmosphere, the alcohol can evaporate, thereby driving  
the equilibrium toward the condensed silicate form.

30

35

1 Dilute aqueous hydrochloric acid can be used to  
catalyze the hydrolysis of the precursor. Other acids  
which can be used as catalysts include mineral acids  
such as sulfuric acid, orthophosphoric acid, and nitric  
5 acid, and organic acids such as trichloroacetic acid,  
formic acid and oxalic acid. The amounts to be used  
vary for each acid, but the optimum quantity can readily  
be determined by a chemist of ordinary skill in the art.  
The action of organic acids generally is slower than  
10 that of inorganic acids.

Hydrolysis of the precursor can also be catalyzed  
by a hydroxyl source which itself is nonreactive with  
the precursor, but which reacts with moisture to  
produce hydroxyl ions, such as described in U. S.  
15 Patent No. 3,653,930, issued to Law et al, and  
incorporated herein by reference. This patent  
describes catalyzing hydrolysis of silicates with a  
hydroxyl source nonreactive with the silicate and  
reactive with moisture to produce hydroxyl ions.  
20 Exemplary of hydroxyl sources are organic amines  
such as mono-, di-, and triethanolamine, diamylamine,  
cyclohexylamine, piperidine, and the like, and  
inorganic hydroxyl sources such as potassium, sodium,  
and lithium hydroxide.

25 A solvent may also be used with the precursor is  
hydrolyzed. Thus, the precursor is dissolved in a  
solvent such as ethanol before hydrolysis. Exemplary  
of the solvents which can be used are those listed in  
Table I of U. S. Patent No. 3,653,930. Preferably,  
30 the solvent is the same alcohol as the alcohol from  
hydrolysis reaction. For example, when the precursor

1 comprises tributyltin ethoxysiloxane, ethyl alcohol  
results from hydrolysis and the preferred solvent is  
ethyl alcohol. In practice of this invention, such  
solvent is distilled from the solution and it is  
5 preferable to recover a single distillate for reuse  
in the process or for other uses without further  
separations.

It has previously been considered appropriate  
to supply a coating composition including a precursor  
10 or prepolymer in a package with a hydrolysis catalyst.  
For example, a precursor can be packaged with a source  
of hydroxyl ions so that upon addition of water,  
hydrolysis and polycondensation can occur. It has  
not been considered appropriate to hydrolyze the  
15 precursor with hydroxyl ion catalysis an appreciable  
time before application as a coating because of the  
possibility of premature gellation and short shelf  
life. When the precursor is hydrolyzed with acid  
catalysis, the precursor, a water miscible solvent,  
20 water, and acid can be packaged together for reducing  
the curing time of the applied coating. In some  
embodiments, the acid catalyzed coating composition  
can be provided in a single container. In the acid  
catalyzed product, it had previously been considered  
25 necessary to prevent evaporation of the alcohol  
product of hydrolysis to prevent premature poly-  
condensation and less than complete hydrolysis of  
the precursor is preferred.

30 It has been found that gellation of the organotin  
siloxane can be inhibited by substantially completely  
hydrolyzing the organotin R-oxysiloxane and replacing

1 the alcohol from the hydrolysis reaction with a water  
immiscible solvent such as xylene. It appears that  
some polymerization occurs in the xylene, forming a  
5 solution of polymeric material, since the solution  
becomes viscous. The polymeric material in the  
solution can be considered for two different ranges  
of tin to silicon ratio. As pointed out above, when  
the ratio of tin atoms to silicon atoms in a polymer  
is less than about 2:5, appreciable cross-linking can  
10 occur for forming solid films suitable as binders in  
coating compositions. When the ratio of tin atoms  
to silicon atoms in a polymer is more than about 2:5,  
steric hindrances inhibit cross-linking and an  
essentially linear polymer is obtained.

15 When the tin to silicon ratio is more than about  
2:5, it appears that linear polymerization of prepolymer  
occurs as alcohol is distilled from the solution,  
resulting in a solution of polymeric material in water  
immiscible solvent where the polymeric material may  
20 be similar to the polymer obtained by evaporating the  
alcohol and forming a film, for example. This appears  
so since the solution is somewhat similar to a solution  
made by redissolving in water immiscible solvent a film  
made by evaporating alcohol from a prepolymer solution.  
25 It is believed, however, that the polymeric material in  
a solution made by mixing water immiscible solvent  
with the water miscible solvent and then distilling  
off the water miscible solvent has greater polymeri-  
zation than a redissolved polymer. The elevated  
30 temperature used for distillation is believed to  
promote added polymerization of the polymeric



1 material. It is desirable to directly transfer from  
a water miscible solvent to a water immiscible solvent  
since appreciably faster and easier than going through  
a solid state.

5 When the tin to silicon ratio is less than about  
2:5, the prepolymer can cross-link when alcohol  
evaporates from a solution. Surprisingly, however,  
when a water immiscible solvent such as xylene is  
added and the alcohol distilled from the solution,  
10 cross-linking is inhibited and a solution containing  
organotin substituted siloxane polymeric material  
results. Some polymerization of the prepolymer is  
believed to occur since viscosity of a xylene solution  
is noticeably higher than viscosity of an original  
15 ethyl alcohol solution. The polymeric material in the  
xylene solution is not completely cross-linked,  
otherwise it would not be retained in solution.  
Neither the exact state of the polymeric material  
nor the reasons for this effect are known. Such a  
20 solution cannot be made by redissolving a solidified  
polymer since the cross-linked polymer is not soluble  
in xylene or similar water immiscible solvents.

Formation of a substantially completely hydrolyzed  
solution of polymeric material in a water immiscible  
25 solvent can be quite advantageous. By replacing water  
miscible solvent with water immiscible solvent, the  
polymeric material can be made compatible with a  
variety of coating ingredients with which it is not  
compatible before hydrolysis and/or in the presence  
30 of ethanol or other water miscible solvents. For  
example, hydrolyzed polymeric material in xylene is

1 compatible with chlorinated rubber coating compositions.  
Further, by this technique, entrapment of residual  
ethanol or other product of the hydrolysis reaction  
in the coating film is prevented. Polymers with high  
5 tin content are particularly susceptible to this  
condition.

Preparation of a solution containing hydrolyzed  
polymeric material can be understood by reference to  
an exemplary embodiment. Thus, for example, tributyltin  
10 ethoxysiloxane is dissolved in a water miscible solvent  
such as ethanol. This precursor is hydrolyzed by adding  
a hydrolysis catalyst and water. Complete hydrolysis  
requires one mole of water per two moles of alkyl and/or  
alkoxyalkyl groups on the precursor. When the hydrolysis  
15 is acid catalyzed, a dilute aqueous solution of acid  
can be slowly added to the solution of siloxane in  
ethyl alcohol with good stirring. The addition can be  
at ambient or elevated temperature up to the temperature  
where decomposition of materials commences. When the  
20 reaction is catalyzed by hydroxyl ions, a source for  
generating hydroxyl ions such as an amine can be added  
to the ethyl alcohol solution of siloxane. Water is  
then slowly added to the well stirred mixture at ambient  
or elevated temperature. Additional ethanol is a  
25 product of the hydrolysis.

A nonreactive or water immiscible solvent such  
as xylene is added before, during, or after the  
hydrolysis. It can be desirable to add the water  
immiscible solvent after hydrolysis in the case of  
30 acid catalysis and before hydrolysis in the case of  
hydroxyl catalysis.

1           When the hydrolysis is complete and the water  
immiscible solvent has been added, temperature is  
raised sufficiently to remove ethanol by distillation.  
The product is a solution of hydrolyzed polymeric  
5           material with a concentration dependent on the amount  
of water immiscible solvent added.

          Although the example employs a specific soloxane  
and specific solvents, it will be apparent that a  
variety of materials as outlined above can be employed.  
10          Preferably, the water miscible solvent is the same  
alcohol as results from the hydrolysis reaction.

          The water immiscible solvent is preferably  
xylene which is compatible with the ethyl alcohol of  
the preferred embodiment, as well as being a good  
15          solvent in coating compositions. Ethyl alcohol can  
be readily distilled from such a mixture. Other  
suitable solvents can be selected from the water  
immiscible solvents set forth in Table I of U. S.  
Patent No. 3,653,930, incorporated by reference  
20          hereinabove. Additional exemplary water immiscible  
solvents include halogenated solvents such as  
methylene chloride, carbon tetrachloride, trichloro-  
ethylene and trichlorotrifluoroethane; various alkanes  
such as pentane, hexane, octane or cyclohexane, or  
25          low melting waxes, some acetates such as sec-  
butylacetate and tert-butylacetate; benzene; naphtha;  
toluene; methyl isobutyl ketone; mineral spirits;  
gasoline; turpentine, lograine, kerosene, and the  
like. The water immiscible solvent preferably has  
30          a higher boiling point than the water miscible solvent

1 or R-alcohol product of hydrolysis so that they can  
be removed by distillation. Other techniques for  
removing the water miscible solvent, such as a molecular  
sieve, can also be employed in some embodiments.

5 Such a solution containing polymeric material can  
be mixed with a variety of ingredients for forming  
compositions for forming marine antifouling coatings.  
A broad variety of solvents, thixotropic agents,  
fillers, pigments, binders, and the like for marine  
10 antifouling coating compositions will be apparent.  
Oil based and water based paints, organic polymer  
coating compositions such as acrylic, polyethylene,  
polypropylene, polystyrene, polyurethane, polyvinyl-  
chloride, chlorinated rubber, alkyd resins, and similar  
15 coating materials can be included. Diluents, fillers,  
and pigments can be included in a coating composition  
such as talc, limestone, diatomaceous earth, clay,  
iron oxides, zinc oxides, lead oxide, titanium,  
dioxide, zinc dust, silica, wollastonite, barites,  
20 barium metaborate, chrome yellow, chrome green, copper,  
copper oxide, and the like. Organic dyes may also be  
used to color the product.

These and other features of the present invention  
will be further understood by reference to the following  
25 Examples.

#### EXAMPLE I

A precursor is formed by reacting 533.2 grams of  
Ethyl Silicate 40 with 623.7 grams of tributyl tin  
30 acetate. Ethyl acetate from the reaction is removed  
by distillation yielding 1000 grams of tributyltin

1 ethoxysiloxane or tributyltin ethyl silicate. This  
precursor is mixed with 500 grams of ethyl alcohol,  
20 grams of 2-ethylaminoethanol and 200 grams of  
5 xylene. This solution is heated to about 50°C and  
stirred vigorously while 61 grams of water is added  
dropwise to the solution over a period of about 15  
minutes. The temperature of the solution is then  
increased to effect distillation of the ethyl alcohol.  
Distillation is complete when 942.5 grams of distillate  
10 is collected. The product, comprising a tributyltin  
substituted siloxane polymeric material in xylene, is  
a viscous liquid.

#### EXAMPLE II

15 A marine antifouling coating composition is  
formulated from a solution containing polymeric  
material prepared in accordance with Example I and  
contains the following ingredients: 98.0 grams of  
tributyltin silicate (from Example I), 77.0 grams of  
20 Allopren X-10 (a chlorinated rubber binder), 9.2  
grams of coal tar, 36.3 grams of ww rosin, 5.6 grams  
of pine oil, 15.8 grams of Shell solvent 1693  
(a petroleum distillate), 3.0 grams of Chevron  
solvent 265 (naphtha), 39.0 grams of xylene, 1.6  
25 grams of methanol, 56.0 grams of zinc oxide, 42.0  
grams of red iron oxide, 35.0 grams of talc, and  
5.4 grams of Bentone 34 (dimethyldioctadecyl ammonium  
bentonite). When this composition is coated on a  
substrate and the solvents evaporate, an adherent,  
30 tough, somewhat resilient marine antifouling coating  
results.

1

EXAMPLE III

5

10

15

20

25

30

35

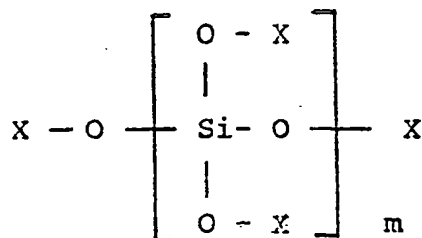
A precursor is formed by reacting 745.2 grams of Ethyl Silicate 40 with 453.3 grams of tributyltin acetate. Ethyl acetate from the reaction is removed by distillation. A solution is formed comprising 200 grams of the resultant tributyltin ethyl silicate in 100 grams of ethanol. The solution is heated to 40°C and stirred vigorously during slow dropwise addition of 17.8 grams of a 2% solution of sulfuric acid in water combined with an equal volume of ethanol. When the addition of this mixture is complete, 50 milliliters of xylene is added to the solution which is then heated to distill the ethyl alcohol. When about 150 milliliters of distillate has been collected, an additional 200 milliliters of xylene is added, distillation is considered complete when a total of 400 milliliters of distillate has been collected. The product is a clear liquid which becomes somewhat cloudy upon cooling. Full cross-linking and precipitation of polymer was not observed. This solution containing polymeric material is useful in a variety of marine antifouling coating compositions.

1 What is claimed is:

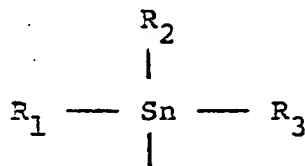
1. A method for preparing a solution containing hydrolyzed organotin siloxane polymeric material  
5 comprising: combining an organotin R-oxy siloxane in which the ratio of tin atoms to silicon atoms is in the range of 1:50 to 1:1, where R represents a group consisting of alkyl and alkoxyalkyl radicals containing less than six carbon atoms, a water  
10 miscible solvent, water, and a hydrolysis catalyst, characterized by including a water immiscible solvent and after hydrolysis of the organotin R-oxy siloxane, removing by distillation the water miscible solvent and R-alcohol from the hydrolysis reaction.  
15
2. A method as recited in Claim 1 wherein sufficient water is combined for substantially completely hydrolyzing the organotin R-oxy siloxane.
- 20 3. A method as recited in one of the precedings claims wherein the water miscible solvent comprises R-alcohol.
4. A method as recited in Claim 3 wherein R is  
25 the ethyl radical.
5. A method as recited in one of the preceding claims wherein the water immiscible solvent comprises xylene.
- 30 6. A method as recited in one of the precedings claims wherein the water immiscible solvent is added after hydrolysis and before distillation.
- 35 7. A method as recited in one of the preceding claims wherein the ratio of tin atoms to silicon atoms in the organotin R-oxy siloxane is less than about 2:5.

1. 8. A method for preparing a solution containing hydrolyzed organotin substituted siloxane polymeric material comprising the steps of:

combining a precursor having the formula:



where m is from about 1 to about 10, each X is independently selected from the group consisting of R and Y, R is selected from the group consisting of alkyl and alkoxyalkyl radicals containing less than about six carbon atoms, and each Y is independently a trisubstituted tin radical having the formula:



where  $\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  are independently selected from the group consisting of alkyl, cycloalkyl, and aryl radicals, and contain in combination up to about eighteen carbon atoms; a water miscible solvent; water; a source of ions selected from the group consisting of hydrogen ion and hydroxyl ion; and a water immiscible solvent having a boiling point higher than the boiling point of the water miscible solvent; and

after hydrolysis of the precursor removing by distillation the water miscible solvent and R-alcohol from the hydrolysis reaction.



1 9. A method as recited in Claim 8 wherein m is  
an average of about five.

5 10. A method as recited in Claim 8 wherein the  
water miscible solvent comprises ethyl alcohol.

10 11. A method for preparing a solution containing  
hydrolyzed organotin siloxane polymeric material  
comprising the steps of:

reacting ethoxysiloxane and a trisubstituted tin  
compound selected from the group consisting of  
tributyltin acetate and bis-tributyltin oxide for  
forming a precursor;

15 dissolving the precursor in ethyl alcohol;  
adding water and a source of hydrolysis  
catalyst selected from the group consisting of  
hydrogen ion and hydroxyl ion to the precursor  
20 solution for forming a hydrolyzed prepolymer in  
solution in ethyl alcohol;

adding a water immiscible solvent to the solution  
of prepolymer in ethyl alcohol; and

removing the ethyl alcohol by distillation.

25 12. A method as recited in Claim 11 wherein the  
water immiscible solvent is compatible with a  
chlorinated rubber binder for a marine antifouling  
coating.

30 13. A method as recited in one of the preceding  
claims wherein the hydrolysis catalyst is hydroxyl  
ion or hydrogen ion.

35 14. A solution comprising a water immiscible solvent  
containing a polymeric material consisting essentially  
of hydrolyzed organotin substituted siloxane, where

- 1 the ratio of tin atoms to silicon atoms in the polymeric material is in the range of from about 1:50 to 2:5.
- 5 15. A solution as recited in Claim 14 wherein the water immiscible solvent comprises xylene.

10

15

20

25

30

35



European Patent  
Office

# EUROPEAN SEARCH REPORT

0051810

Application number

EP 81 10 9130.5

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,X	<p><u>US - A - 4 080 190</u> (G.H. LAW et al.)</p> <p>* column 4, line 18 to column 8, line 47; column 10, line 44 to column 13, line 4; column 13, examples 1 to 3; column 14, example 8; column 16, table 3, example 19 *</p> <p>---</p>	<p>1-5,</p> <p>7-15</p>	<p>C 08 G 77/18</p> <p>C 08 G 77/06</p> <p>C 09 D 5/14</p> <p>A 01 N 55/04</p> <p>C 08 L 83/08</p> <p>C 09 D 3/00</p>
A	<p><u>US - A - 3 392 036</u> (G.D. McLEOD)</p> <p>* column 3, lines 4 to 59 *</p> <p>---</p>	<p>1,3,5</p>	<p>TECHNICAL FIELDS SEARCHED (Int. Cl. 7)</p>
D,A	<p><u>US - A - 3 653 930</u> (G.H. LAW et al.)</p> <p>* column 5, table 1 *</p> <p>---</p>	<p>3,5</p>	<p>A 01 N 55/04</p> <p>C 07 F 7/04</p> <p>C 08 G 77/00</p> <p>C 08 L 83/08</p> <p>C 09 D 3/00</p> <p>C 09 D 5/00</p>
A	<p>FARBE UND LACK, Vol. 83, No. 12, 1977</p> <p>J. LORENZ "Bewuchsschutz an Schiffen - eine Standortbestimmung"</p> <p>pages 1072 to 1079</p> <p>* page 1078, paragraphs 9-1,9-2 *</p> <p>-----</p>		<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant</p> <p>A: technological background</p> <p>C: non-written disclosure</p> <p>P: intermediate document</p> <p>T: theory or principle underlying the invention</p> <p>E: conflicting application</p> <p>D: document cited in the application</p> <p>L: citation for other reasons</p>
<p>X The present search report has been drawn up for all claims</p>			<p>&amp;: member of the same patent family, corresponding document</p>
Place of search		Date of completion of the search	Examiner
Berlin		01-02-1982	IDEZ

**THIS PAGE BLANK (USPTO)**